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TI - Thermoplastic hydrogenated graft copolymers for films and adhesives

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AB - Hydrogenated graft copolymer of formula A(B)x (in which A is main polymer chain derived from alpha-olefins, dienes and/or monovinyl aromatic hydrocarbons, pref. polybutadiene, styrene-butadiene copolymer or polyvinyl aromatic; B is linear polymer chain grafted onto A and derived from anionically polymerisable monovinyl aromatic hydrocarbons and/or opt. substituted conjugated dienes, pref. polystyrene or butadiene-styrene copolymer; x is positive integer). Complete or partial hydrogenation is carried out to give monovinyl aromatic-or vinylcyclohexane-substituted ethylene graft copolymer. Hydrogenation pref. takes place in presence of catalyst.

Graft copolymerisation can be controlled precisely, so that hydrogenated copolymer has required physical properties, including higher m.pt. and better oxidation stability than unhydrogenated polymer.

Dimensional stability is higher for completely hydrogenated than for partly hydrogenated material.

Products can be used as films, with good clarity and toughness, adhesives and rubbery to rigid thermoplastic materials.



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⑮ CANADIAN PATENT

⑯ HYDROGENATED GRAFT COPOLYMERS

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Granted to Borg-Warner Corporation, Chicago, Illinois, U.S.A.

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The instant invention is directed to vinylaromatic-substituted ethylene graft copolymers and vinylcyclohexane-substituted ethylene graft copolymers prepared by the hydrogenation of substrate graft copolymers.

The substrate graft polymers that are hydrogenated to prepare the copolymers of this invention are of the general formula



wherein the backbone polymer, A, of the graft polymer is 10 prepared from monomers selected from the group consisting of alpha-olefins, dienes, substituted dienes, monovinylaromatic hydrocarbons and substituted monovinylaromatic hydrocarbon monomers and mixtures thereof. The backbone polymer in all cases contains some degree of aliphatic or aromatic unsaturation. The uniform pendant side chains, (B), grafted to the backbone polymer, A, are comprised of linear polymeric segments prepared from monomers polymerizable by anionic means. X is defined as a positive integer.

The monomers grafted to the backbone of the graft 20 copolymers are not restricted in number and may be one or more, however, are restricted to those that are anionically polymerizable or copolymerizable. As mentioned, x is a positive integer and the number of polymer chains is not limited. Examples of monomers that may be used in preparing the grafted polymers, (B), are monovinylaromatic hydrocarbon monomers such as styrene, paramethyl styrene and the like; vinyl naphthalene, as well as conjugated dienes, i.e., butadiene, isoprene, piperylene, dimethyl butadiene, methyl pentadiene, cyclohexadienes and the like.

30 After preparation of the aforementioned graft polymer, the polymer is subjected to hydrogenation either wholly or in part to provide the monovinylaromatic-substituted

ethylene graft polymers or substituted vinyl cyclohexane substituted ethylene graft copolymers of this invention.

The compositions of the instant invention are characterized by the method of preparation of the graft copolymeric materials prior to hydrogenation. In the preparation of the graft polymers, prior to hydrogenation, the backbone polymeric chain may be formed by any convenient process as, for examples, anionic, cationic, free radical or Ziegler-Natta methods. The backbone polymer is thereafter dissolved or suspended in an inert hydrocarbon solvent and treated with a suitable reagent such as an organo-alkali metaldiamine complex to introduce active organometallic sites along the backbone chain. After the sites are formed on the backbone, the desired grafting monomer or monomers are added which anionically polymerize directly onto the backbone at the preformed metallic sites to produce uniform linear graft branches.

It will be understood that utilizing the methods set forth herein, a variety of compositions may be obtained and the amount of monomer grafted on the polymeric backbone can be closely controlled. The number of sites available on the backbone of the polymeric substrate is determined in all cases by the amount of organometallic complex employed to metalate the backbone using the equation:

$$\text{Number of sites} = \frac{\bar{M}_n \text{ of backbone}}{\text{wt. backbone}} \times \text{moles complex}$$

wherein \bar{M}_n is defined as the number average molecular weight of the backbone polymer. It is possible to tailor any given graft polymer to obtain a desired number and length of side chains on the selected backbone, by utilizing the relationship

between the molecular weight of the backbone, the molecular weight of each of the side chains and the number of sites as set forth in the expression:

$$\text{Graft } \bar{M}_n = \bar{M}_n \text{ backbone} \times \frac{\text{wt. \% Graft Monomer (s)}}{\text{wt. \% Backbone Polymer}} \times \frac{1}{\text{Number of sit}}$$

wherein \bar{M}_n is defined as the number average molecular weight.

10

It should be noted that the specific graft polymers that form the substrates for the preparation of the products of this invention are also novel as a result of the specific tailored side chains placed on the substrate backbone.

The preparation of previous graft polymers, e.g., those prepared by emulsion, solution or bulk-free radical, radiation initiated, or mechanical shear initiated polymerizations, have given non-uniform products contaminated with homopolymer and mixtures of non-uniform graft structures often containing "gelled", i.e., cross-linked and insoluble materials, which has limited their utility.

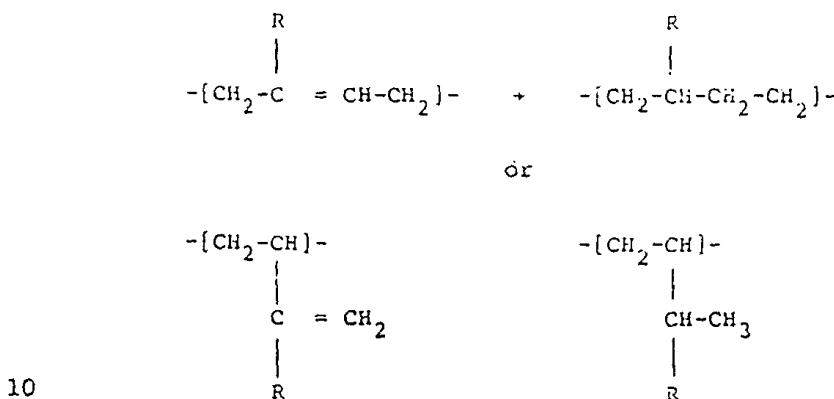
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The aliphatic and aromatic unsaturation of the graft copolymers can be hydrogenated utilizing such catalysts as Raney nickel, noble metals and those formed by the reaction of transition metal carboxylate salts with alkylaluminum compounds. By manipulating the parameters of the hydrogenation process such as hydrogen pressure, temperature, time, catalyst, etc., one may effect hydrogenation of the aliphatic unsaturation only, or the complete hydrogenation of substantially all of the unsaturated sites. The hydrogenated graft polymers that result are completely unlike any other graft copolymer structures heretofore known in the art.

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The reduction of the polymeric diene in the graft copolymers to remove ethylenic unsaturation will result in

substituted polyethylene structures, as set forth below

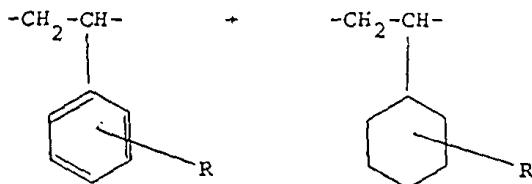


Equation I

wherein R is selected from the group consisting of hydrogen and alkyl containing one to ten carbon atoms.

The reduction of aromatic unsaturation provides cyclohexane structures. The structures referred to herein, to be used as a portion of the backbone or graft polymer chains of the monovinylaromatic hydrocarbon variety are shown below

20



Equation II

wherein the R group is a lower alkyl (1-10 C atoms) or hydrogen group and the reduction of the aromatic ring of the monovinylaromatic hydrocarbon polymer segments will provide a cyclohexyl or substituted cyclohexyl group as a substituent on the polymeric chain.

30

As a consequence of the precise control of the graft copolymerization process for the preparation of the substrate

copolymer the physical properties of the resultant hydro-
genated graft copolymers can be precisely tailored. More-
over, these substrate graft copolymers are readily hydro-
genated owing to their homogeneous and linear graft branches
and the substantial absence of gel and cross-linked chains
as compared to the previously known graft copolymers. The
hydrogenated graft polymers exhibit higher melting temperatures
and substantially better oxidative stability than the unhydro-
genated graft copolymers. Additionally, fully hydrogenated
10 graft copolymers exhibit higher dimensional stability at
elevated temperatures than do the corresponding partially
hydrogenated graft copolymers. The hydrogenated graft polymers
of this invention may be used as films which exhibit good
optical clarity and toughness as well as adhesives and a
variety of other thermoplastic products ranging from rubbery
to rigid products.

The following examples are illustrative of specific
embodiments of the present invention.

Example 1

20 Styrene Grafted Onto Polybutadiene

Polybutadiene (30g), prepared by anionic polymeriza-
tion in cyclohexane to a molecular weight of 113,000 (calculated
from its specific viscosity of 1.39 in Toluene ($c=0.1$ dl/g, $t=25C$)),
was treated with 0.79 m moles of sec-butyllithium and 0.79 m moles
of tetraethylene diamine (TMEDA) for two hours at room temperature
with careful exclusion of air and moisture. The amount added was
sufficient to provide three graft sites per polymer chain.

On completion of the metalation, 3.33g of pure styrene
monomer were added to the complex, whereupon initiation and
30 polymerization of the styrene occurred. After stirring in the
absence of air and moisture at 50C overnight to ensure complete

polymerization, the polymer solution was quenched by addition of isopropanol.

To a one-third portion of the solution of 1,4-polybutadiene were added 10 mls of a 0.1 mole cyclohexane solution of cobalt octoate/triethyl aluminum (1:3) hydrogenation catalyst. The mixture was placed in a pressure vessel and treated with a constant flow of 50 psig hydrogen while stirring and heating to 75°C. After one hour, the resulting gelled mass was removed from the vessel, washed while hot to remove catalyst, and coagulated in isopropanol. The product, amounting to 11g, had these properties set forth in Table I, hereinbelow, and exhibited no olefinic unsaturation as determined by IR measurement.

The properties for additional partially hydrogenated styrene-butadiene graft copolymers are given in Table I as Examples 2-16. Where the substrate backbone polymer is described as having 1,2-polybutadiene character, the anionic polymerization of the butadiene was accomplished by techniques known to the art as, for example, carrying out the polymerization in the presence of polar compounds. The method is illustrated in the following procedure.

Example 5

Sufficient butadiene was anionically polymerized in a cyclohexane solution containing 0.27 m moles of sec-butyllithium (and 0.27 m moles TMEDA as the polar solvent), to yield 30g of polybutadiene having a molecular weight of 110,000. The polybutadiene was then treated with 2.72 m moles of sec-butyllithium and 2.72 m moles of TMEDA for two hours at room temperature. This amount of complex was sufficient to provide 10 graft sites per polymer chain.

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On completion of the metalation, 10.0g of pure styrene monomer were added to the complex, whereupon initiation and polymerization of the styrene occurred. After stirring in the absence of air and moisture overnight to ensure complete polymerization, the polymer solution was quenched by addition of isopropanol. The graft copolymer, on isolation, had a 1,2-polydiene structure corresponding to 60% of the backbone as measured by known infrared techniques, and the efficiency of grafting was 88% as determined by acetone extraction.

10

Hydrogenation of the substrate, substantially as carried out in Example 1, produced a polymer having no detectable olefinic unsaturation. The polymer exhibited those properties set forth in Table I.

20

It will be apparent to those skilled in the art that further controlled variations in 1,2 diene content of the backbone are possible by varying the proportion of the polar agent employed, and further that other polar agents known in the art, as well as other polymerization methods may be employed to accomplish controlled levels of 1,2 structures in the backbone polymer.

Example 17

Cis-1,4-polybutadiene was prepared from 1,3-butadiene by polymerization in benzene-cyclohexane mixed solvent using a cobalt octoate-diethyl aluminum chloride catalyst. The polymer was extracted to remove catalyst residues and precipitated in alcohol and dried. The molecular weight was 76,000 and the cis isomer content was 93.6%.

30

Cis polybutadiene (30g), prepared as set forth above, was dissolved in cyclohexane and treated as in Example I, but with sufficient sec-butyllithium/TMEDA, to provide 10 metal

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sites on the polymer chain. To this was added 30g of styrene monomer as before. After polymerization at 50°C, the polymer solution was

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TABLE I
PARTIALLY HYDROGENATED GRAFT COPOLYMERS

Ex	Graft				Backbone		HYDROGENATED PRODUCT				
	Chain	\bar{M}_W	Wt%	Sites	Type		\bar{M}_W	Yield Psi	Ultimate Psi	E δ	Remarks
1	Styrene	4200	10	3	1,4-polybutadiene		113,000	1300	3000	500	Flexible plastic
2	Styrene	1250	10	10	1,4-polybutadiene		113,000	1400	2600	450	Flexible plastic
3	Styrene	5250	25	7	1,4-polybutadiene		110,000	1600	2800	380	Flexible plastic
4	Styrene	3700	25	10	178 1,2-polybutadiene	110,000	570	40 0	510	Rubbery	
5	Styrene	3700	25	10	608 1,2-polybutadiene	110,000	160	1380	640	Rubbery	
6	Styrene	2725	34	10	1,4-polybutadiene	54,500	2000	2200	260	Flexible plastic	
7	Styrene	2725	34	10	178 1,2-polybutadiene	110,000	980	2250	360	Rubbery	
8	Styrene	16,600	34	3	608 1,2-polybutadiene	100,000	100	260	260	Soft, rubbery gum	
9	Styrene	8300	34	6	648 1,2-polybutadiene	100,000	400	1300	470	Snappy rubber	
10	Styrene	5000	34	10	608 1,2-polybutadiene	100,000	280	1770	675	Snappy rubber	
11	Styrene	8000	42	10	1,4-polybutadiene	110,000	2420	2920	300	Flexible plastic	
12	Styrene	8000	42	10	608 1,2-polybutadiene	110,000	560	1700	470	Snappy rubber	
13	Styrene	2300	42	35	1,4-polybutadiene	113,000	2130	2680	300	Flexible plastic	
14	Styrene	11,300	50	10	1,4-polybutadiene	113,000	2800	2800	320	Flexible plastic HDT* 51°C	
15	Styrene	87,670	70	3	1,4-polybutadiene	113,000	----	4200	7	Rigid	

TABLE I (cont'd)

Ex	Chain	Graft	Backbone			HYDROGENATED PRODUCT			
			\bar{M}_w	Wt%	Sites Type	\bar{M}_w	Yield psi	Ultimate Esi	E $\%$
16	Styrene	26,200	70	10	1,4-polybutadiene	113,000	----	4260	6
17	Styrene	6,700	50	10	cis polybutadiene	67,000	2920	2310	Rigid, HDT*74°C
18	Styrene	8,000	42	10	cis polyisoprene	110,000	400	1100	500
19	Vinyl toluene	3700	34	15	1,4-polybutadiene	110,000	1700	2300	Rubbery
20	40% styrene-butadiene block	9500	95	10	Styrene	5,000	810	770	10
21	Styrene	2100	30	10	20% styrene-butadiene styrene block copolymer	50,000	3030	3420	310

*HDT--heat distortion temperature under 264 lb. load.

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quenched with isopropanol. A one-quarter portion of the polymer solution, treated with hydrogenation catalyst and reduced as in Example I, yielded polymer having no residual olefinic unsaturation, and exhibiting physical properties set forth in TABLE I.

It will be apparent to those skilled in the art that a variety of additional diene monomers such as isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene and the like, and other vinylaromatic monomers such as vinyl toluene, 10 α -methylstyrene and the like, may be employed in preparing substrates for hydrogenation. That these may also exhibit useful properties is illustrated in Examples 18 and 19.

The monomers useful in the preparation of graft copolymers may also be combined, so that the backbone itself is a block or random copolymer. Further, the sequential or combined employment of two or more monomers in preparing the graft chains will result in block or random copolymeric graft chains. Examples 20 and 21 illustrate two of the great many possible combinations, and further demonstrate 20 the useful properties which result upon partial hydrogenation.

Example 22

Full Hydrogenation

A polymer prepared as in Example I, but with sufficient sec-butyllithium and TMEDA to produce 7 graft sites in place of the originally described three graft sites, was similarly treated with hydrogenation catalyst and placed in an autoclave. Reduction was carried out at 4000 psig hydrogen pressure and 250°C, to prepare 11g of a polymer having no residual olefinic or aromatic unsaturation, as determined by IR measurements.

30 The properties of this material are given in TABLE II. Additional selected examples of fully hydrogenated graft copolymers are also given in TABLE II.

TABLE II
FULLY HYDROGENATED GRAFT COPOLYMERS

Ex	Graft				Backbone		Hydrogenated Product			
	Chain	\bar{M}_W	Wt%	Sites	Type	\bar{M}_W	Yield psi	Ultimate psi	E _b psi	Remarks
22	Styrene	1800	10	7	1,4-polybutadiene	113,000	1500	3000	420	Flexible plastic
23	Styrene	5000	25	7	1,4-polybutadiene	105,000	2200	2900	380	Flexible plastic
24	Styrene	3900	25	10	1,4-polybutadiene	118,000	1800	2900	400	Flexible plastic
25	Styrene	5000	34	7	63% 1,2-polybutadiene	60,000	740	2400	500	Rubbery
26	Styrene	20,000	50	3	1,4-polybutadiene	60,000	----	2300	17	Flexible plastic, HDT 67°C
27	Styrene	12,000	50	10	1,4-polybutadiene	120,000	----	2900	36	Flexible, HDT 65°C
28	Styrene	13,000	65	10	1,4-polybutadiene	70,000	----	2200	25	Rigid, HDT 83°C
29	Styrene	49,000	70	7	1,4-polybutadiene	145,000	----	3900	7	Rigid, HDT 120°C

The foregoing examples are representative of the variety of graft copolymers that may be achieved. It is apparent that a highly desirable feature of the present invention is the degree of control possible in the preparation of tailored graft polymers. Thus, the properties of the copolymers may be tailored to provide either flexible or rigid polymeric materials.

Alternatively, by selective control of 1,2 content, introduction of a desired degree of elastomeric character 10 is possible. Further, full hydrogenation may be employed to impart superior heat resistance characteristics to these copolymers.

The examples have set forth specific embodiments of the graft polymers of this invention to illustrate the different polymeric compositions, however, the examples are not meant to limit the invention in any way.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A thermoplastic graft copolymer prepared by the hydrogenation of a polymeric substrate graft polymer represented by the formula:



wherein "A" is a polymeric backbone prepared from monomers selected from the group consisting of conjugated dienes, monovinyl aromatic hydrocarbons and mixtures thereof and wherein "B" is a pendant linear polymeric chain grafted on said "A" backbone by anionic polymerization and wherein "B" is prepared from monomers selected from the group consisting of conjugated dienes and monovinyl aromatic hydrocarbons wherein "x" is a positive integer.

2. The thermoplastic hydrogenated graft polymer of Claim 1 wherein substantially all of the aromatic and olefinic unsaturation has been removed by hydrogenation.

3. Claim 1 wherein substantially all of the olefinic unsaturation has been removed by hydrogenation.